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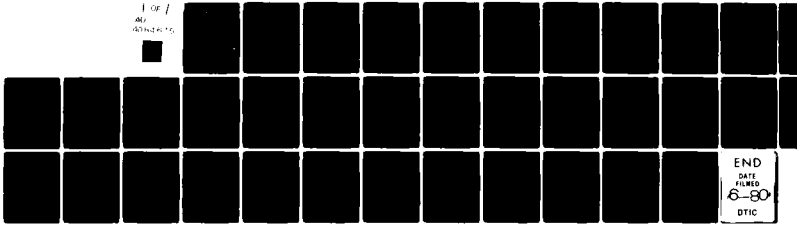

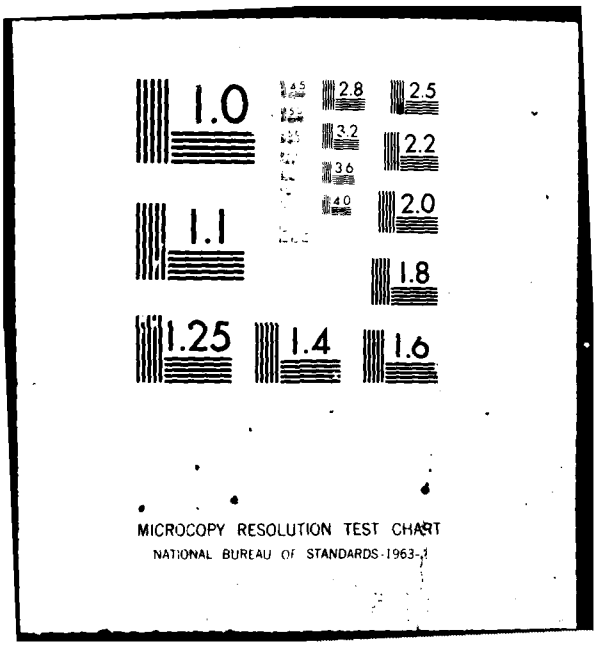
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IONIC MECHANISMS OF CARBON FORMATION IN FLAMES

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The objective of this program is to establish a chemical mechanism of soot formation which will serve as a basis for practical solutions to the smoke problem in jet engines. An experimental program is currently underway at AeroChem to study soot formation in premixed laminar flames to test proposed chemical mechanisms, in particular the hypothesis that soot nucleates on chemically formed ions whose growth is thermochemically favored and proceeds by very rapid ion-molecule reactions. Mass spectrometric measurements of positive ion concentration profiles in rich and sooting acetylene and benzene flames show many similarities and

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some distinct differences. As sooting is approached by increasing the equivalence ratio, the concentration of large ions with mass greater than 300 grows rapidly.

A detailed mechanism by which these ions grow to form soot particles has been developed for acetylene combustion. Computer simulations using this mechanism qualitatively describe many features experimentally observed in flames including the rapid growth of heavy ions.

An analytical study of the literature data on the effects of fuel structure on the critical composition at which soot forms is underway. The results differ considerably from currently accepted trends.

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I. INTRODUCTION AND RESEARCH OBJECTIVES

The formation of soot in jet combustors is undesirable because it increases heat transfer to the engine walls, creates a tactically disadvantageous smoke trail, and is of environmental concern due to possible health hazards. These problems will become more prevalent as "new fuels," i.e., those derived from coal, tar sands, and shale, are used since these fuels are characterized by more aromatic constituents, higher molecular weights, and higher C/H ratio than current fuels. Each of these properties increases the smoking tendency of jet engines.

It is the objective of this program to further the understanding of these phenomena by providing a chemical mechanism which can be used in model predictions to solve practical problems. The hypothesis which the experimental program seeks to test is that ions produced via chemi-ionization serve as nuclei for the formation of soot particles. Evidence has accumulated[1] which indicates that the normal neutral radical chemical processes of hydrocarbon combustion reach a bottleneck where the thermochemistry and kinetics prevent the production of larger molecules on the pathway to soot formation. The ion chemistry, normally only a minor feature of a combustion system, is proposed as a route whereby rapid ion-molecule kinetics, rapid ion structural rearrangements, and favorable thermochemistry lead to rapid growth of large polycyclic ions and particle formation.

These objectives are being pursued by mass spectrometric measurements of ion concentration profiles in low pressure premixed flat flames of several representative fuels. Specifically we are seeking to:

a. Determine the effects of fuel structure (representative of petroleum and coal derived fuels) on soot formation and on the ion chemistry in laboratory flames.

b. Determine whether and how chemical additives affect nucleation (initial particle formation) or coagulation and growth (larger particle forming processes) of soot by determining the effects of chemical additives on ionic processes in flames.

c. Study the sooting characteristics of flames of mixed hydrocarbons for the purpose of ascertaining synergistic effects and developing a means for predicting the smoking tendency of real fuel systems.

d. Interpret, as the work progresses, the results from the above experiments, and data in the literature, in terms of an ionic and a free radical mechanism of soot formation in flames and compare these mechanisms to determine their relative importance.

e. Interpret the above data and mechanisms in terms of the potential effects of new fuels on soot formation in air breathing engines, and possible means of minimizing soot formation in air breathing engines.

II. RECENT PROGRESS AND PROGRAM STATUS

This is the third annual report on a program begun on 1 January 1977. Recent work has concentrated on detailed measurements and interpretation of the ion chemistry in rich and sooting premixed acetylene oxygen and benzene oxygen flames at 2.0 kPa (15 Torr), and on a comparative study of the quantitative effects of fuel structure on sooting tendency in premixed and diffusion flames using existing data from a variety of literature sources. This work has produced three publications, one of which is included in the Appendix; the other two are in the final stages of preparation and will be available within the next two months. These present a detailed discussion of our results and progress; only brief additional details will be given here.

Continued mass spectrometric work, partially described in the Appendix, has emphasized obtaining further details of the ion chemistry of flames of the two fuels (selected primarily because of the availability of other data on these flames), and, in particular, confirming the dual-peaked behavior of ion concentration profiles in near-sooting and sooting flames. We are convinced now that this behavior cannot be an experimental artifice of the sampling probe or burner interactions since it is observed over a broad range of experimental conditions of pressure, temperature, and flow velocity. Several explanations have been proposed, each of which appears to be unlikely when compared to experimental data. It is possible that negative ions (or particles) are replacing electrons as the negative charge carrier slowing the ion recombination rate and therefore increasing the concentration of positive ions. This question remains unanswered and we are preparing to measure negative ion concentrations in these same flames.

Additional recent progress has been made in the development of a reaction mechanism with which to simulate the flame combustion processes and test proposed routes of soot formation. This has been pursued in two areas. First,

thermodynamic properties were needed for species proposed to take part in the reaction mechanism. We have gathered as much data as possible from the scientific literature but mostly have used the methods of group additivity[2] to estimate the standard heats of formation, entropies, and heat capacities of selected C_3 to C_{19} hydrocarbon ions. With this data it is possible to calculate heats of reaction and equilibrium constants to aid in mechanistic development.

Secondly, we have tested qualitatively the predictions of an ion chemistry scheme in producing the species which we observe experimentally. To this end we have used a one dimensional adiabatic flow tube simulation program to perform computer modeling of an acetylene flame. This program does not consider the diffusional or heat transfer processes important to ignition in the flame front, but should quite adequately provide information about the post-ignition chemistry of the system. A relatively modern neutral-radical mechanism for C_2H_2 combustion[3] was extended to consider chemi-ion production, ion growth, and charged species recombination, resulting in a scheme of 63 reactions of 34 species. A preliminary series of calculations has produced several results. First, the primary ion (i.e., produced from neutral reactants) in this scheme, $C_3H_3^+$, shows neither the highest concentration or the earliest peak. Second, the computed ion profiles are very sensitive to the heats of formation (calculated) for the larger ions, e.g., $C_7H_7^+$. These values are uncertain over a wide range. Experimental measurements of selected thermochemical properties are needed. Lastly, we are able to compute extremely rapid growth of the largest ions, e.g., $C_{19}H_{11}^+$, considered in this mechanism. It would be very interesting next to include consideration of particles into this model.

A considerable amount of recent work has also been applied to design and construction of a new mass spectrometer and flame sampling apparatus designed to extend our capability to measure ions up to mass 5000 in these flames. We hope to follow the growth of incipient soot particles over the whole size range until coagulation of individual particles takes over and other techniques become more applicable.

The effect of molecular structure on soot formation in premixed, diffusion, and jet engine combustion is an extremely important problem in assessing the impact "new fuels" will have on engine performance, in determining engine design to use the new fuels, and in determining the ideal new fuel(s) for jet

engines. We would define the term ideal new fuel as the fuel structure toward which the fuel chemist must work in converting a high C/H feedstock material to a useful fuel which may also have a high C/H ratio. This is comparable to the considerations which took place in the early days of the development of the reciprocating engine which led to the concept of octane number. For the above reasons, and to guide us in picking interesting (and thus important) fuels for study, we have been analyzing the literature on the effect of fuel structure in both premixed and diffusion flames. We have developed a quantitative scale of 0 to 100 to make quantitative comparisons between fuels and between various investigators possible. This is something that has not been possible before. The details will be available in a paper to be submitted to Combustion and Flame shortly. The results are rather different from the generally accepted qualitative effects of fuel structure on sooting.

III. REFERENCES

1. Calcote, H.F., "Mechanisms of Soot Nucleation in Flames," Combust. Flame, to be submitted April (1980).

2. Stein, S.E., Golden, D.M., and Benson, S.W., "Predictive Scheme for Thermochemical Properties of Polycyclic Aromatic Hydrocarbons," J. Phys. Chem. 81, 314 (1977).

3. Olson, D.B. and Gardiner, W.C., Jr., "Combustion of Methane in Fuel-Rich Mixtures," Combust. Flame 32, 151 (1978).

IV. PERSONNEL

The authors are pleased to acknowledge the assistance of Dr. D.M.. Manos in the study of the effects of fuel structure, and L.R. Koenig and M. Thompson who assisted with the experiments.

V. PUBLICATIONS AND PRESENTATIONS

The following publications were prepared during the year.

1. Olson, D.B. and Calcote, H.F., "Ions in Fuel Rich and Sooting Acetylene and Benzene Flames," submitted to The Eighteenth Symposium (International) on Combustion, to be held 17-22 August 1980.

2. Calcote, H.F. and Manos, D.M., "The Effect of Fuel Structure on Soot Formation in Flames," in preparation for submission to Combust. Flame.
3. Calcote, H.F., "Mechanisms of Soot Nucleation in Flames," A Review to be submitted to Combust. Flame in April 1980.

The following presentations were given during the year by H.F. Calcote:

1. "Mechanisms of Soot Formation" at the Ballistics Research Laboratory, Aberdeen, MD, 10 January 1979.
2. "Soot Formation in Flames - A Survey," H.F. Calcote, AIAA 17th Aerospace Sciences Meeting, New Orleans, LA, 15-17 January 1979.

In addition the authors are in frequent communication with other specialists in soot formation and combustion. Interest in this program has been expressed, for example, by the following:

1. Roguemore, W.M., AF Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio, several conversations and phone calls.
2. Personnel at NASA (Lewis) whom H.F. Calcote visited on 20 June 1979.
3. Attendees at the Annual Conference on Fire Research sponsored by the Center for Fire Research, National Bureau of Standards, August 22-25, 1979.
4. Gann, R.G. and attendees at an invited discussion on Soot Formation Chemistry, National Bureau of Standards, 18-19 December 1979.
5. Farmer, R.C., Louisiana State University, Baton Rouge, LA, several conversations and phone calls.
6. Glassman, I., and attendees at the Princeton University Weekly Seminars in Fluid Mechanics and Combustion.
7. D'Alessio, A., at the Universita P. le V. Tecchio, Napoli, Italy.
8. Michaud, P. and Barassin, A. of the Centre de Recherches sur la Chemie de la Combustion et des Hautes Temperatures at Unversite d'Orleans, Orleans, France.

VI. NEW TECHNOLOGY

The idea for an electrostatic probe to detect incipient soot formation was conceived by D.B. Olson and H.F. Calcote. The possibility of using the change in current-voltage characteristics of an electrostatic probe to detect soot production just prior to its occurrence was recognized. It is envisioned that this device could be used to control the fuel/air ratio of a two-staged combustor where it is desirable to operate the first stage as fuel-rich as practical but with no production of soot. It would also be applicable to controlling the fuel/air ratio in air breathing jet engines to maintain soot emissions just below the point of visible soot production or in controlling the quantity of injected additives for soot control to minimize deleterious effects of the additives on the engine. A small program (6 months) has been initiated at AeroChem by NASA (Lewis) to determine the feasibility of the idea.

APPENDIX

IONS IN FUEL RICH AND SOOTING ACETYLENE AND BENZENE FLAMES

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ABSTRACT

Flame ion profiles from low pressure rich and sooting acetylene/oxygen and benzene/oxygen flames are discussed in terms of their importance in soot nucleation mechanisms. As both flames approach sooting the predominant ion $C_3H_3^+$ is replaced by large positive ions with mass greater than 300. The profile of these large ions is found to correspond with a previously identified class of "soot precursor" species. The dual maxima in ion concentration vs distance profiles observed in sooting flames are discussed.

The data are consistent with an ionic mechanism of soot formation.

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* Prepared for publication in Eighteenth Symposium (International) on Combustion.

I. INTRODUCTION

The formation of soot in combustion of hydrocarbon fuels has received much attention, yet the basic chemical processes controlling the transition from gas-phase species to particles remain unclear. In a recent review of the mechanism of soot formation in flames[1] the evidence was assembled for an ionic nucleation mechanism based upon chemi-ions. The chemi-ions CHO^+ and $C_3H_3^+$ were the key to the initial growth of molecular species to large polycyclic aromatic ions which ultimately became incipient soot particles. Detailed steps in the process were suggested. It is thus important to understand the ion chemistry of fuel-rich flames in order to verify this process and to explain the key chemical steps to soot formation. We here report mass spectrometric measurements of ion concentration profiles in fuel-rich and sooting low pressure premixed acetylene- and benzene-oxygen flames. Acetylene was chosen for study because it is the most extensively studied sooting flame so our results can be compared to previous data to obtain a detailed picture of the process. Benzene with the same C/H ratio was chosen as representative of aromatic substances whose tendency to soot is markedly greater than aliphatic substances and because aromatic substances will be important as "new fuels". It should be noted that acetylene is unique in having a very low tendency to soot in premixed flames, so from that point represents a poor choice. It is planned to study more typical hydrocarbons in future work.

Many similarities and some distinct differences are found between the two flames; the basic trend being the predominance of $C_3H_3^+$ in non-sooting flames with large aromatic ions growing in concentration very rapidly as the critical equivalence ratio, ϕ_c, for sooting is approached.

In the benzene flame front oxygen-containing aromatic ions are also observed but downstream the ions in acetylene and benzene flames are the same. Ions with $300 < \text{mass} \gtrsim 1000$ amu become dominant very early in both flames at ϕ_c.

II. EXPERIMENTAL

The low pressure flame apparatus and ion sampling quadrupole mass spectrometer, shown in Fig. 1, have been previously described.[2] Briefly, the flames were stabilized on a 12 cm diam flat flame burner and were surrounded by a fuel-rich annular shield flame 16 cm diam to prevent air or combustion product entrainment. Gases were metered by a syringe pump. The liquid benzene was sprayed into a flash evaporator and the vapor fed to the burner-mixing chamber through heated lines. The mass spectrometer sampling cone was constructed from 316 stainless steel with a 90° outer angle and a 0.25 mm orifice. Ion profiles through the flame were obtained by moving the burner with respect to the mass spectrometer sampling cone.

The majority of the results were obtained from acetylene/oxygen and benzene/oxygen flames at 15 Torr although some work was performed at 20 Torr. The unburned gas velocity at the burner was 50 cm s^{-1} in all the work reported here. Detailed individual ion species profiles were measured for masses up to 300 at equivalence ratios above and below the critical equivalence ratio, ϕ_c, for soot formation as determined by the appearance of the yellow-orange continuum soot emission. In addition the spectrometer was operated as a high-pass mass filter and profiles were recorded of ions with mass larger than 300 up to the cutoff of the filter, estimated to be about mass 1000. Ion currents are reported

instead of ion concentrations because of the difficulties in quantitatively calibrating the instrument.

III. RESULTS

Representative ion spectra from rich non-sooting acetylene and benzene flames are shown in Fig. 2 taken at a distance of 1 cm from the burner surface in the blue-green reaction zone which extends from about 0.5 to 1.5 cm. The essential features for the acetylene spectrum are the high concentration of $C_3H_3^+$ and the following series of peaks spaced every 13 or 14 mass units. Only odd number ion masses are observed while for neutral species sampled from sooting flames the number of hydrogens is even.[1] Other large peaks, for example mass = 63, 91, and 165 correspond to $C_5H_3^+$, $C_7H_7^+$, and $C_{13}H_9^+$. In these rich flames H_3O^+, the dominant ion in near stoichiometric flames, is observed only at low concentrations.

The spectrum shown for benzene, Fig. 2, is atypical in that beyond the flame zone the observed mass spectrum rapidly becomes very similar to that observed in the acetylene flame. Figure 2 shows ions characteristic of the early benzene oxidation zone. Unique peaks are observed at mass 95, 109, 131, etc., with only a small amount of mass 39, although at 2 cm from the burner the concentration of $C_3H_3^+$ dominates the spectrum. These unique benzene ions are identified as oxygen-containing aromatic species $C_6H_7O^+$, $C_7H_9O^+$, $C_9H_7O^+$, etc. Notable is the lack of species smaller than C_6 indicating little ring opening has occurred at this time.

Figures3 and 4 show additional data for these same two flames in the form of concentration profiles vs distance from the burner surface for selected important species and the 300 < mass < 1000 group identified

as > 300. Note in Fig. 3 the early appearance of mass 165, 239, and > 300 ions in addition to mass 39. The equivalence ratio, ϕ, of this flame was considerably below the critical equivalence ratio, ϕ_c, at the sooting point (ϕ = 2.0 vs ϕ_c = 2.7). Similar data are shown in Fig. 4 for a benzene flame just below the critical equivalence rato for soot formation (ϕ = 1.80 vs ϕ_c = 1.85). Several profiles show dual maxima; the first in the flame front and the second just beyond the point where soot emission is first observed visually. The signal from large ions increases markedly with increasing ϕ. This dual peak behavior is characteristic of both fuels near and beyond sooting and has also been observed by Delfau, Michaud, and Barassin.[3] It should be noted that the same ions occur in both peaks.

The dramatic increase in large ion cencentration at the expense of smaller ions is the most significant change that occurs in the mass spectra as the flames are made rich and finally produce soot. Figure 5 shows the profiles for the > 300 group of ions from six acetylene flames. A hundredfold greater peak concentration is obtained in a ϕ = 3.0 flame compared to the ϕ = 1.75 flame, accompanied by a corresponding decrease in concentration of small ions (not shown). Overall the total ion concentrations remains nearly constant over the wide range of equivalence ratios investigated. Figure 5 also demonstrates the decay of the first ion peak and the growth of the second ion peak as soot is produced. It should be remarked that soot does not form--by visual observation of the well known yellow appearance--abruptly in acetylene flames but rather slowly over a range of equivalence ratios of 2.5 to 2.7. In benzene the appearance of soot as the equivalence ratio is increased is very sudden and very reproducible.

The variation in peak ion concentrations as a function of equivalence ratio for the two fuels is shown in Figs. 6 and 7. We find it significant that at the soot point, indicated in the figures, the large ion concentration, i.e., > 300 amu reaches the same level in both flames even though the equivalence ratios at which this occurs are very different for the two fuels.

IV. DISCUSSION

The ion profiles of acetylene and benzene flames exhibit many similarities and some distinct differences. The basic trend is for $C_3H_3^+$ to dominate in rich non-sooting flames with larger species becoming increasintly more important as the soot point is approached by increasing the equivalence ratio. In a strongly sooting flame (yellow-orange in color) these ions are replaced by ions with mass > 300. The most important species in addition to $C_3H_3^+$ are masses 63, 65 ($C_5H_3^+$, $C_5H_5^+$), 89, 91 ($C_7H_5^+$, $C_7H_7^+$), 165 ($C_{13}H_9^+$), and 239 ($C_{19}H_{11}^+$). Table I shows the species observed at two positions in each flame, corresponding nominally to first peak and second peak compositions. In addition a suggested structure for each ion is given; The mass spectrometer only identifies the mass. First looking at the non-oxygen-containing ions, the small ions other than $C_3H_3^+$ have C/H ratios corresponding to molecules with conjugated double or triple bonds. For C_6 and larger species aromatic structures are assumed to become more and more dominant. Aromatic structures are chosen because of their higher stability and the stability of ions to rapidly rearrange to the more stable structures. Beyond C_{10} fused ring structures are observed. A mechanism which explains the essential features of the observed ion spectra has been

formulated. The primary ions are assumed to be formed by the usual flame chemi-ionization reactions

$$CH + O = CHO^+ + e^-$$

$$CH^* + C_2H_2 = C_3H_3^+ + e^-$$

followed by rapid charge transfer from CHO^+ to H_2O to give H_3O^+ or by several reaction paths to give additional $C_3H_3^+$.[3] If $C_3H_3^+$ is allowed to grow by reaction with only the three major neutral species, C_2H_2, C_2H_4, and C_2H, the following sequence of reactions would occur:

$$C_3H_3^+ + \begin{cases} C_2H_2 \rightarrow C_5H_5^+ \\ C_4H_2 \rightarrow C_7H_5^+ \\ C_2H \rightarrow C_5H_3^+ + H \end{cases}$$

followed by continuing reaction of C_2H, C_2H_2, and C_4H_2 with each ion produced by previous reactions. Only exothermic reactions in the forward direction are considered. If this type of addition to the ions is continued with all rates assumed equal then the ion distributions would be dependent upon the concentrations of C_2H_2, C_4H_2, and C_2H (assumed to be 100:10:1)[5] and the number of reaction channels. Several observed features are predicted by this mechanism: large concentrations of the 89-91 and 63-65 pairs; higher concentrations of 103, 115, 129, and 153 than 101, 113, 127, and 151; and mass 165 being the main ion larger than $\approx$ 110.

The benzene ions observed at 2 cm are very similar to those from acetylene. The spectrum at 1 cm is strikingly different, however, with each of the unique ions in the benzene flame identified as containing an oxygen atom. Other flame studies[6,7] have identified C_6H_6O as a neutral intermediate in rich benzene flames present in significant concentration. It is difficult to speculate on the mechanism of formation of ions in benzene flames because so little is known about benzene combustion

including the identity of the reaction which fractures the ring structure. Nevertheless some of the unique ions can be accounted for as follow:

$$C_6H_6O + CHO^+ \rightarrow C_6H_7O^+ + CO$$
$$95 \text{ amu}$$

$$C_6H_6O + C_3H_3^+ \rightarrow C_9H_7O^+ + H_2$$
$$131$$

$$C_9H_7O^+ + C_2H_2 \rightarrow C_{11}H_9O^+$$
$$157$$

$$C_9H_7O^+ + C_4H_2 \rightarrow C_{13}H_9O^+$$
$$181$$

At about ϕ_c double peaked profiles are observed, located at about 1 cm and 2 cm distances (Figs. 3, 4, and 5). In the leaner flames (ϕ = 1.75 and 2.0) the $>$ 300 ions show a sharp peak at 1 cm with a very rapid decay. This may be due to a higher rate of recombination with electrons for larger ions, see also the decay rate of 239 amu. As the flame becomes richer (Fig. 5), and begins to soot the first peak gives way to a second peak which becomes very large

Mass 39 is the dominant ion in leaner flames, decaying slowly, with its maximum located at about 2 cm which indicates primary ions are still being produced up to this point in the flame. Beyond the soot point mass 39 shows only a very small sharp peak at 1 cm. The intermediate mass ions show intermediate behavior between mass 39 and the $>$ 300 ions.

Similar observations are true for benzene flames at 2 cm where the ion behavior can be divided into three categories (39, ions $<$ 300, and $<$ 300). Double peaks are observed with mass 39 dominating in the leaner flames and large ions dominating in sooting flames.

The reason for the double peaks is not clear. They do not appear to be an experimental artifice. The second peak arises further downstream than the leaner mixture first peak and includes the same ion species as the first peak. It is not just a shift in location. The total number of charged particles is not significantly larger when the second peak appears; it may increase slightly, the data are not that definitive because of an unknown variation in mass spectrometer throughput with mass. Flames with dual maxima are always sooting or near sooting and therefore contain particles which can be thermally ionized if they are larger than mass 10^4 or so[1] for these specific flames. These, however, are not the species being observed, and charge transfer from a small charged particle, P^+, to a molecular or radical species, M

$$P^+ + M = M^+ + P$$

is unlikely since the ionization potential of the molecule, M, is higher than that of the particle and the ions contain an odd number of hydrogens and the neutral species observed[8] contain an uneven number of hydrogens. Alternatively the process

$$PH^+ + M = MH^+ + P$$

is thermodynamically unfavored but cannot be completely eliminated at this time. The observed ions are the same in the first and second peaks; not what would be expected from radically different production processes. One possible explanation would be a reduced loss rate of ions leading to a secondary increase in concentration. Since $C_3H_3^+$ and the neutral building blocks are still present at high concentrations at the second peak location, the ion growth processes are still producing larger ions. If the recombination was suddenly reduced by electron attachment to particles, a second rise in species concentration would occur. There is some

evidence that only positively charged particles are present,[9,10] but the data may not be applicable to the flame front, and even downstream we think it is very possible that a significant concentration of negative particles, less than the concentration of positive particles, could have been overlooked. In a recent paper Homann[11] reported the presence of negative ions in similar flames.

The relationship between flame ion chemistry and the formation of soot is not clear, although a good case can be made for chemi-ions as the precursors of soot. We find large ions formed early in rich flames and see their concentrations fall very rapidly. In near sooting flames the concentration of these species remains high and there is an abrupt change from small ions to large ions. It is difficult to explain these ions as a result of the soot particles or the transfer of protons from chemi-ions such as $C_3H_3^+$ to large molecules being formed in a neutral reaction sequence to soot. The thermodynamics are unfavorable. The large ions can be explained by very rapid exothermic ion-molecule reactions and it is easy to extrapolate these growing by the same processes to incipient soot particles. The energetics are favorable.

An additional argument for chemi-ions as precursors for soot formation is obtained by comparing our results, Fig. 8, for the > 300 ion profile in a 20 Torr $\phi = 3.5$ C_2H_2/O_2 flame with data from other workers measured in the same flame. Homann and Wagner[12] identified a class of species, other than polyaromatic hydrocarbons which had a unique profile, and called them soot "precurors". The >300 ion profile from our work is seen to correspond closely with Homann and Wagner's precursor peak. The decay shape is somewhat different, possibly since our ion profile includes a broader mass class than the "precursors". Also shown

on the figure are the "large" positive ion profile measured by Howard and coworkers.[13] Their mass class was defined only as > 300 amu but it probably weights larger ions than in our measurement because of the different measurement techniques. Thus, a progression from small ions to large ions to soot or charged soot would be apparent.

V. CONCLUSIONS

Results of a mass spectrometric study have been reported of the ions present in rich and sooting low pressure acetylene and benzene flames. A significant difference in the ion spectrum is observed between non-sooting and sooting flames, with the increasing dominance of ions with mass larger than > 300 amu as the flame is made fuel richer. Dual maxima, observed in concentration vs distance profiles from sooting flames, are not fully understood. High concentrations of oxygen-containing aromatic ions, not found elsewhere, are observed in the flame front of the benzene system.

Although we are not able, at the present, to quantitatively demonstrate that an ionic mechanism of soot formation dominates over other possible mechanisms, the data and arguments presented here are consistent with such a soot formation pathway. Problems encountered with other routes have been discussed elsewhere,[1,14] and the evidence continues to indicate the importance of an ionic mechanism wherein nucleation can occur by reactions producing chemi-ions and subsequent rapid exothermic ion-molecule growth.

ACKNOWLEDGMENT

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Table 1

Ions identified in acetylene and benzene flames

Relative concentrations indicated by number of *. Ions unique to benzene indicated by *.

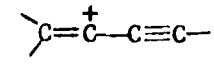
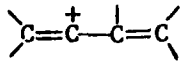
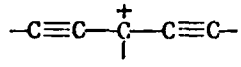
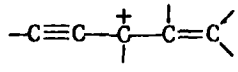
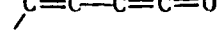
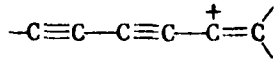
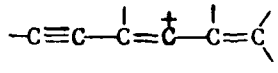
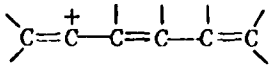
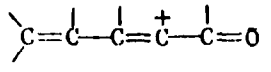
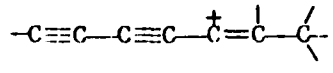
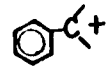
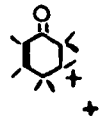
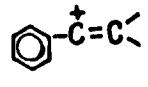
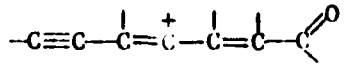
Mass	Species	Structure	C_2H_2/O_2, ϕ = 2.0		C_6H_6/O_2, ϕ = 1.8	
			1 cm	2 cm	1 cm	2 cm
19	H_3O^+					*
39	$C_3H_3^+$		***	***	*	***
51	$C_4H_3^+$					**
53	$C_4H_5^+$		*	*	*	*
63	$C_5H_3^+$			**		***
65	$C_5H_5^+$		*	*		
67	$C_4H_3O^+$				*	
75	$C_6H_3^+$			*		**
77	$C_6H_5^+$		*	*		*
79	$C_6H_7^+$			*		
81	$C_5H_5O^+$				**	
89	$C_7H_5^+$		*	**		**
91	$C_7H_7^+$		**	**	**	**
95	$C_6H_7O^+$				**	
103	$C_8H_7^+$		*	*		**
105	$C_7H_5O^+$				**	

TABLE I (Continued)

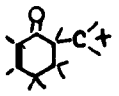
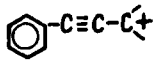
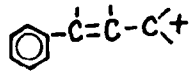
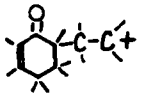
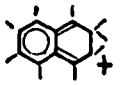
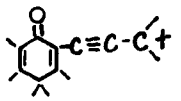
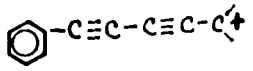
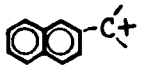
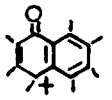
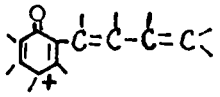
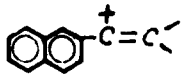
Mass	Species	Structure	C_2H_2/O_2, ϕ = 2.0		C_6H_6/O_2, ϕ = 1.8	
			1 cm	2 cm	1 cm	2 cm
109	$C_7H_9O^+$				**	
115	$C_9H_7^+$			*		
117	$C_9H_9^+$		*			*
119	$C_8H_{11}O^+$				**	
129	$C_{10}H_9^+$		*	*		*
131	$C_9H_7^+$				***	
139	$C_{11}H_7^+$			*		
141	$C_{11}H_9^+$		*	*		*
143	$C_{10}H_7O^+$				**	
145	$C_{10}H_9O^+$				**	
153	$C_{12}H_9^+$		**	**		

TABLE I (Continued)

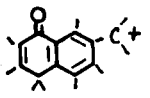
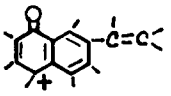
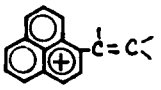
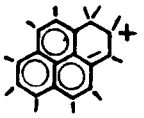
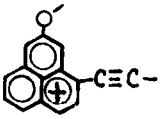
Mass	Species	Structure	C_2H_2/O_2, ϕ = 2.0		C_6H_6/O_2, ϕ = 1.8	
			1 cm	2 cm	1 cm	2 cm
157	$C_{11}H_9O^+$				**	*
165	$C_{13}H_9^+$		***	***	***	***
169	$C_{12}H_9O^+$				**	
179	$C_{14}H_{11}^+$		*	*	*	
181	$C_{13}H_9O^+$				**	*
191	$C_{15}H_{11}^+$		**	*	**	*
203	$C_{16}H_{11}^+$		*	*	*	*
205	$C_{15}H_9O^+$				**	
215	$C_{17}H_{11}^+$		*	*	**	*

TABLE I (Continued)

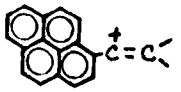
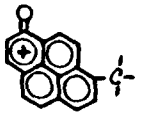
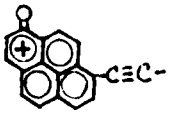
Mass	Species	Structure	C_2H_2/O_2, ϕ = 2.0		C_6H_6/O_2, ϕ = 1.8	
			1 cm	2 cm	1 cm	2 cm
217	$C_{16}H_9O^+$				*	
227	$C_{18}H_{11}^+$		*	*	*	*
231	$C_{17}H_{11}O^+$				*	
239	$C_{19}H_{11}^+$		**	*		
241	$C_{18}H_9O^+$				*	**

FIGURE CAPTIONS

Fig. 1. FLAME ION SAMPLING MASS SPECTROMETER

Fig. 2. ION SPECTRA FOR ACETYLENE AND BENZENE FLAMES

Data taken 1 cm above burner correspond to "first peak" compositions at 15 Torr. C_2H_2/O_2, ϕ = 2.0. Mass signal is offscale at 150; benzene/O_2, ϕ = 1.8.

Fig. 3. ION PROFILES FOR ACETYLENE/OXYGEN NON-SOOTING FLAME

15 Torr, ϕ = 2.0, calculated adiabatic flame temperature, T_a = 2300 K.

Fig. 4. ION PROFILES FOR BENZENE/OXYGEN NEARLY SOOTING FLAMES

15 Torr, ϕ = 1.8, calculated adiabatic flame temperature, T_a = 1900 K.

Fig. 5. EFFECT OF EQUIVALENCE RATIO ON > 300 amu ION PROFILES FOR ACETYLENE/OXYGEN FLAMES

Ions 300 > amu > 1000, 15 Torr. Transition to sooting occurs between ϕ = 2.5-2.75.

Fig. 6. EFFECT OF EQUIVALENCE RATIO ON PEAK ION CURRENTS FOR ACETYLENE/OXYGEN FLAMES

15 Torr.

Fig. 7. EFFECT OF EQUIVALENCE RATIO ON PEAK ION CURRENTS FOR BENZENE/OXYGEN FLAMES

15 Torr.

Fig. 8. CONCENTRATION PROFILES FOR AN ACETYLENE/OXYGEN FLAME 20 Torr, ϕ = 3.5 (after Ref. 1); ions > 300, this work--use current scale, all others use number density scale. "Large Ions" and "Charged Soot" particles from Prado and Howard[13]; "Soot" from Wersborg, Yeung, and Howard[10] and Bonne, Homann, and Wagner[5]; "Precursors" and "$C_{14}H_8$", typical of polycyclic aromatic hydrocarbon, from Homann and Wagner[8].

79-71A

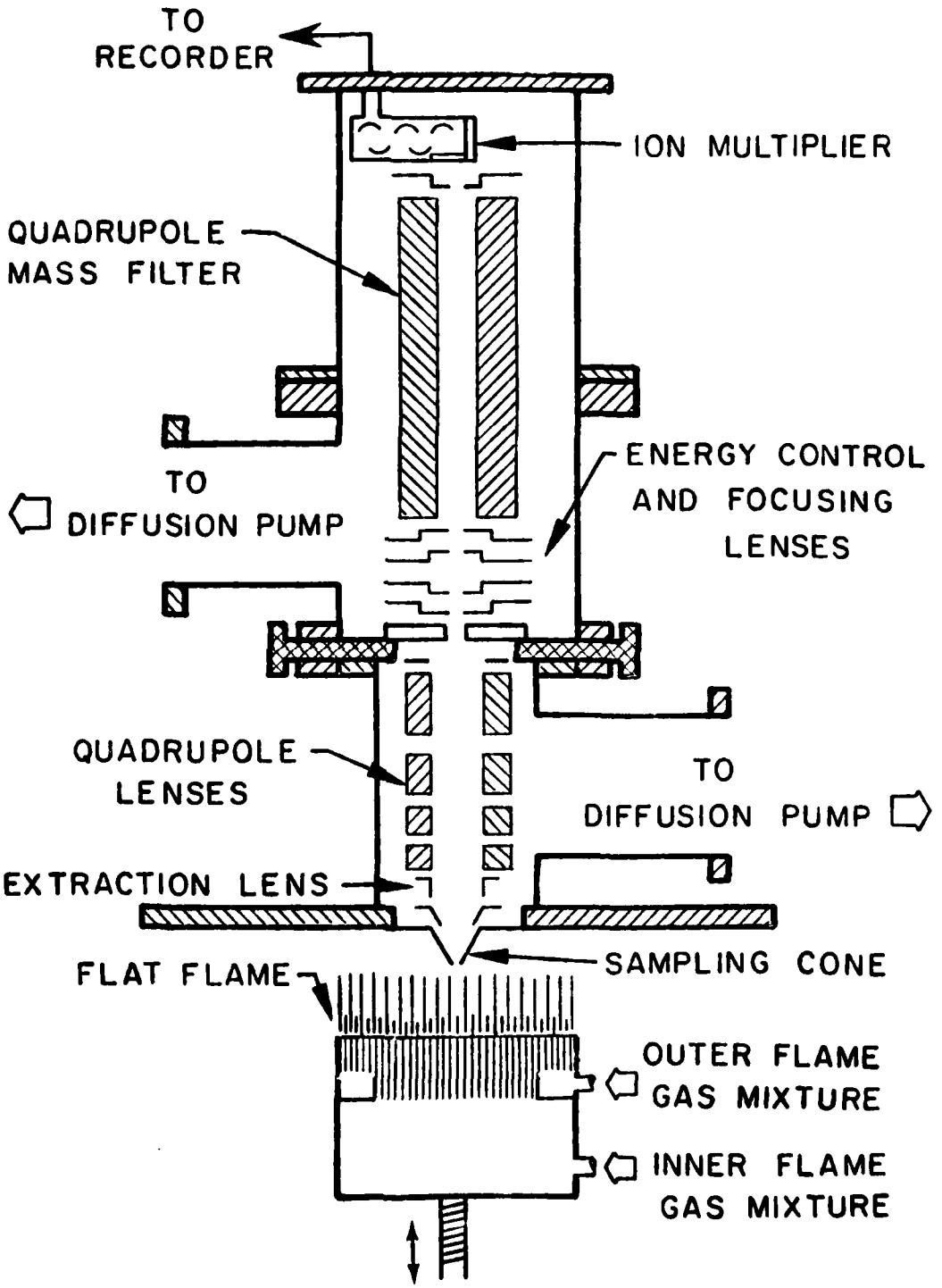

TO
RECORDER
ION MULTIPLIER
QUADRUPOLE
MASS FILTER
TO
DIFFUSION PUMP
ENERGY CONTROL
AND FOCUSING
LENSES
QUADRUPOLE
LENSES
TO
DIFFUSION PUMP
EXTRACTION LENS
FLAT FLAME
SAMPLING CONE
OUTER FLAME
GAS MIXTURE
INNER FLAME
GAS MIXTURE

FIG. 1

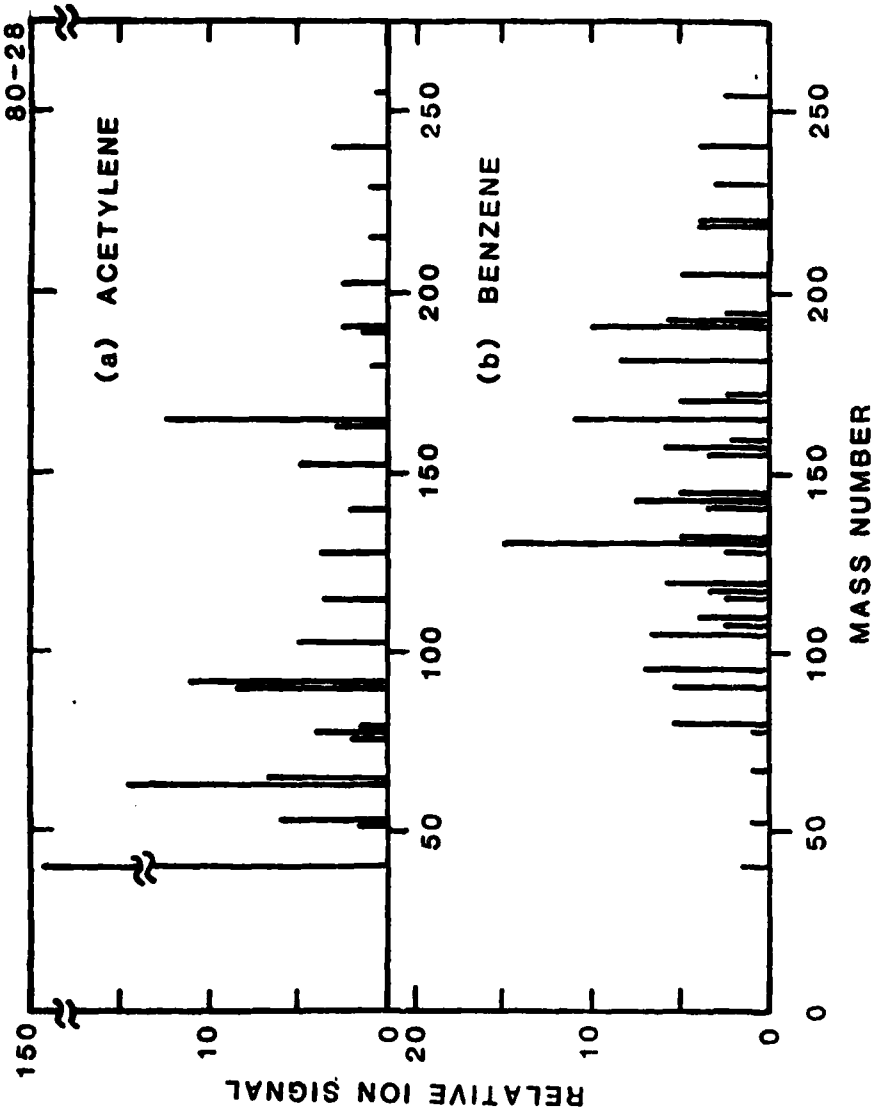

80-28
(a) ACETYLENE
(b) BENZENE
RELATIVE ION SIGNAL
MASS NUMBER
150
10
0
20
10
0
0
50
100
150
200
250
0
50
100
150
200
250

FIG. 2

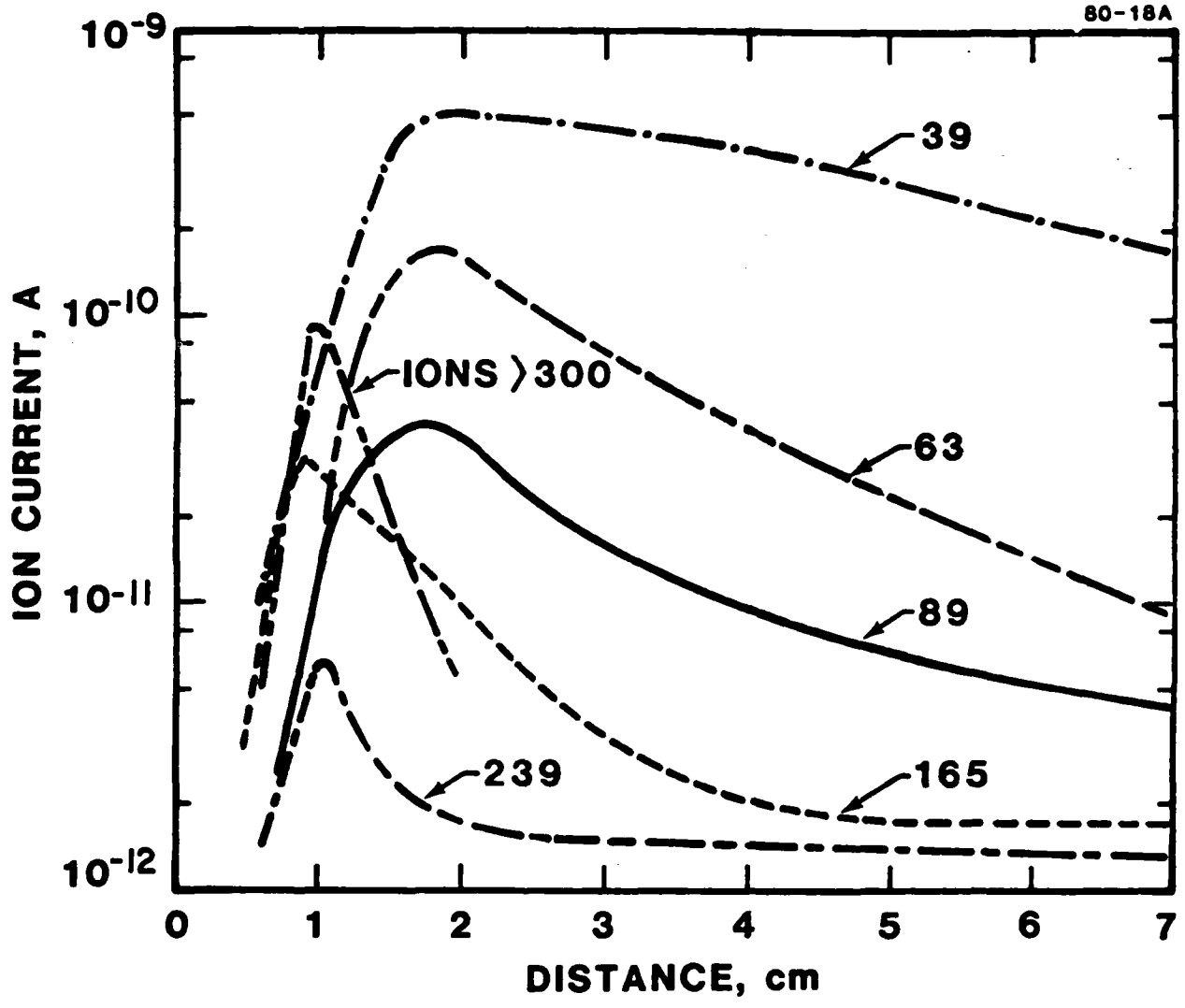

80-18A
10^{-9}
10^{-10}
10^{-11}
10^{-12}
ION CURRENT, A
39
IONS >300
63
89
239
165
0
1
2
3
4
5
6
7
DISTANCE, cm

FIG. 3

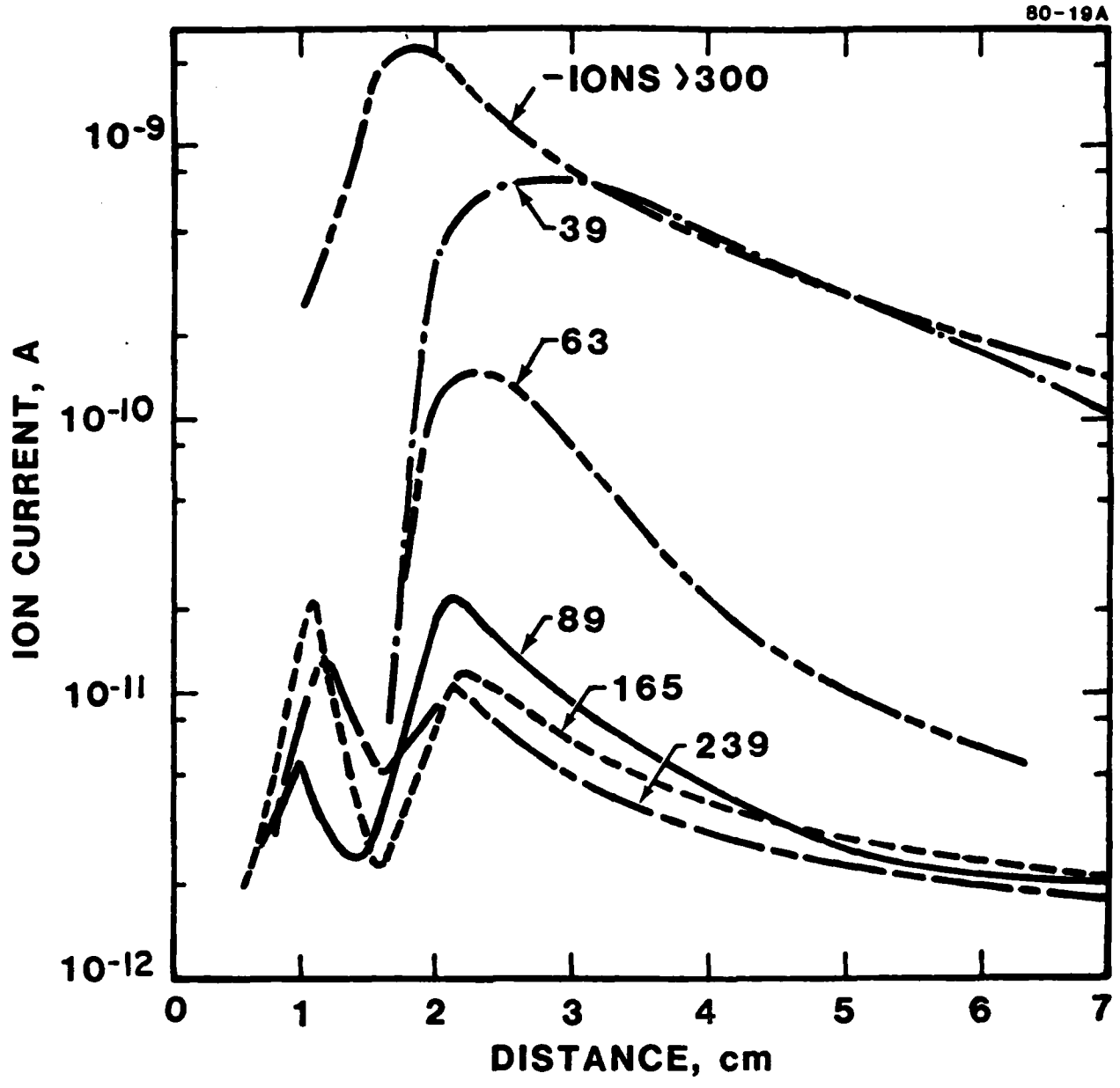

80-19A
IONS >300
39
63
89
165
239
ION CURRENT, A
10-9
10-10
10-11
10-12
0
1
2
3
4
5
6
7
DISTANCE, cm

FIG. 4

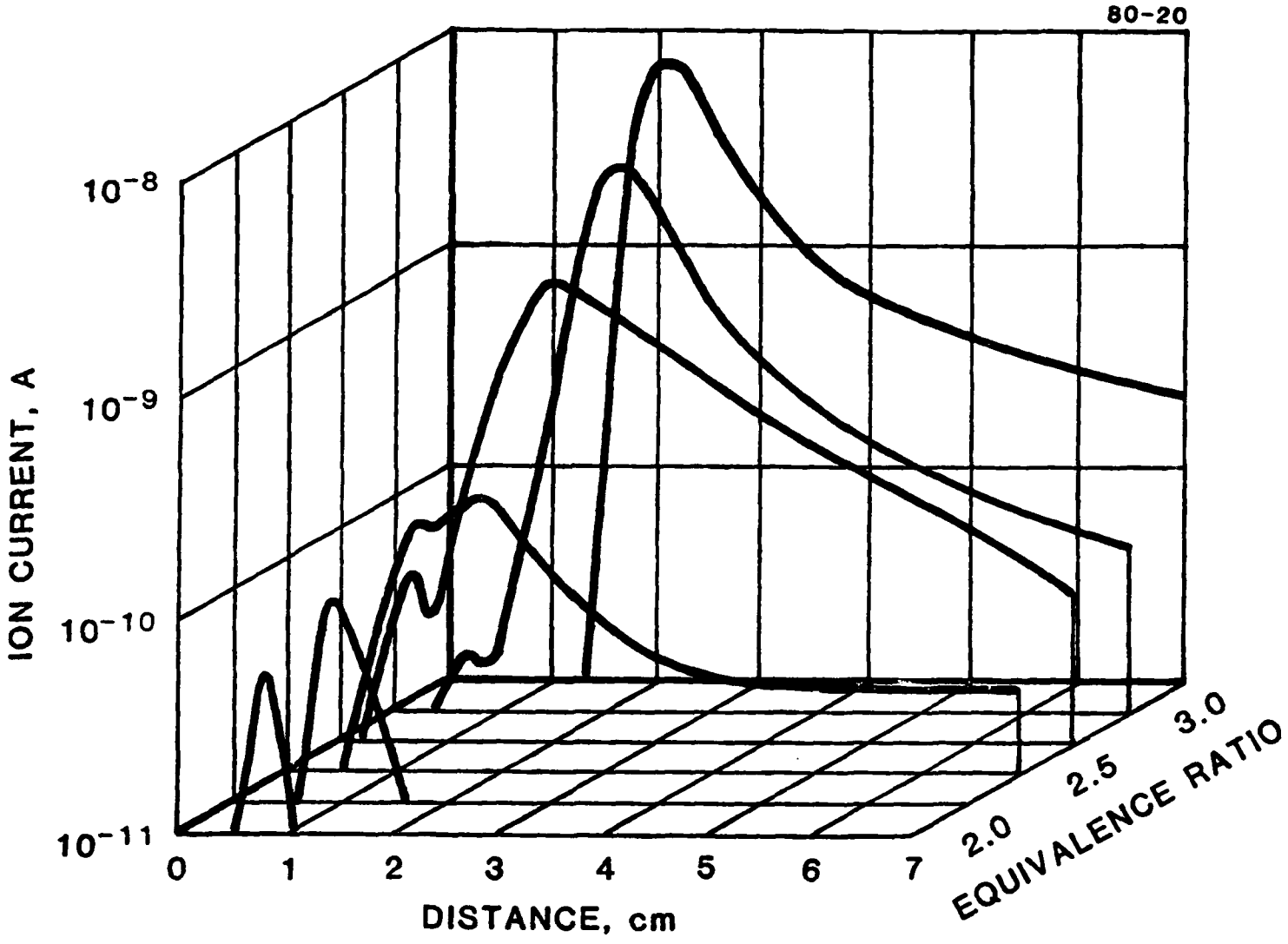

80-20
10^{-8}
10^{-9}
10^{-10}
10^{-11}
ION CURRENT, A
0
1
2
3
4
5
6
7
DISTANCE, cm
2.0
2.5
3.0
EQUIVALENCE RATIO

FIG. 5

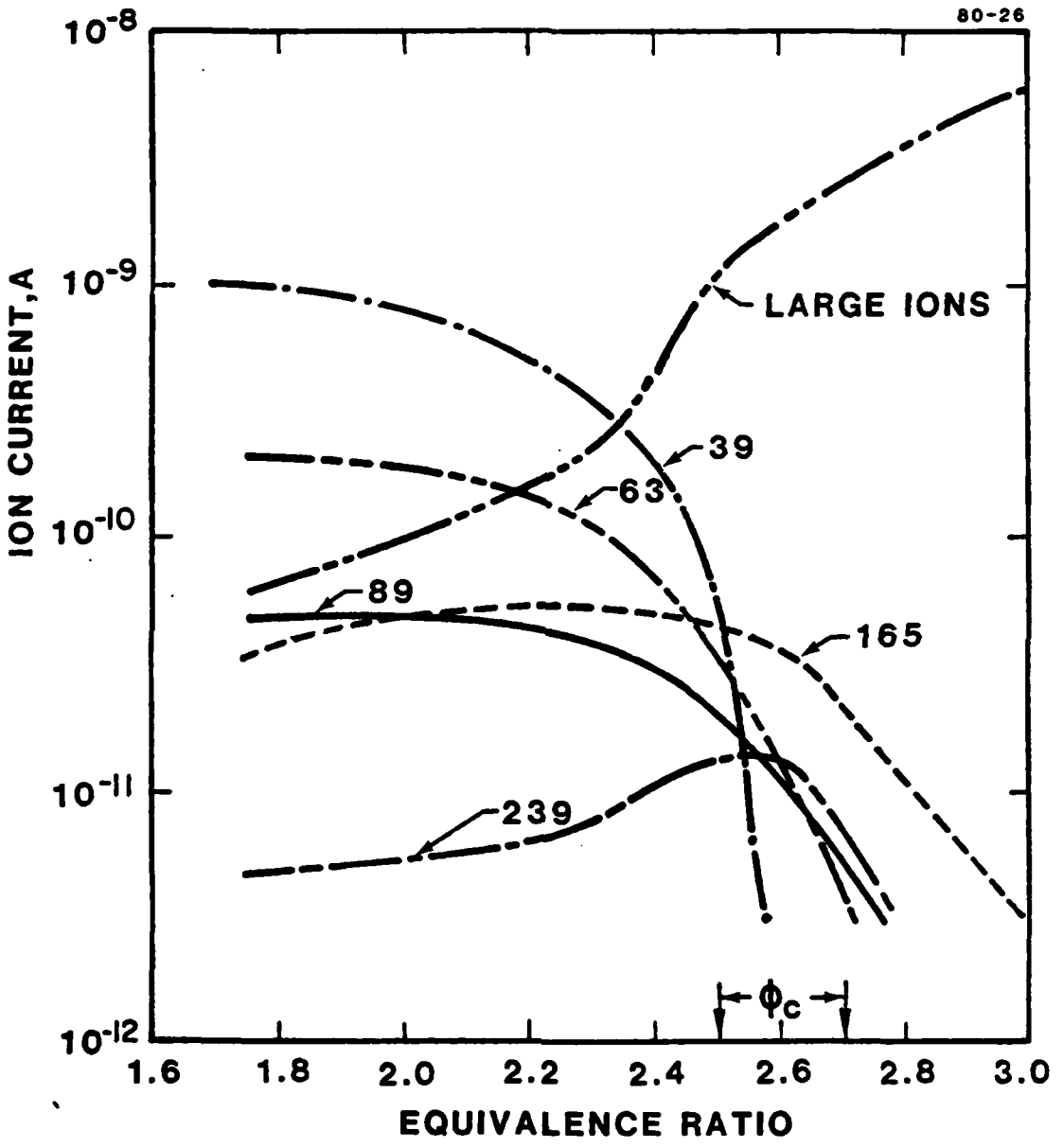

80-26
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
ION CURRENT, A
LARGE IONS
39
63
89
165
239
ϕ_c
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
EQUIVALENCE RATIO

FIG. 6

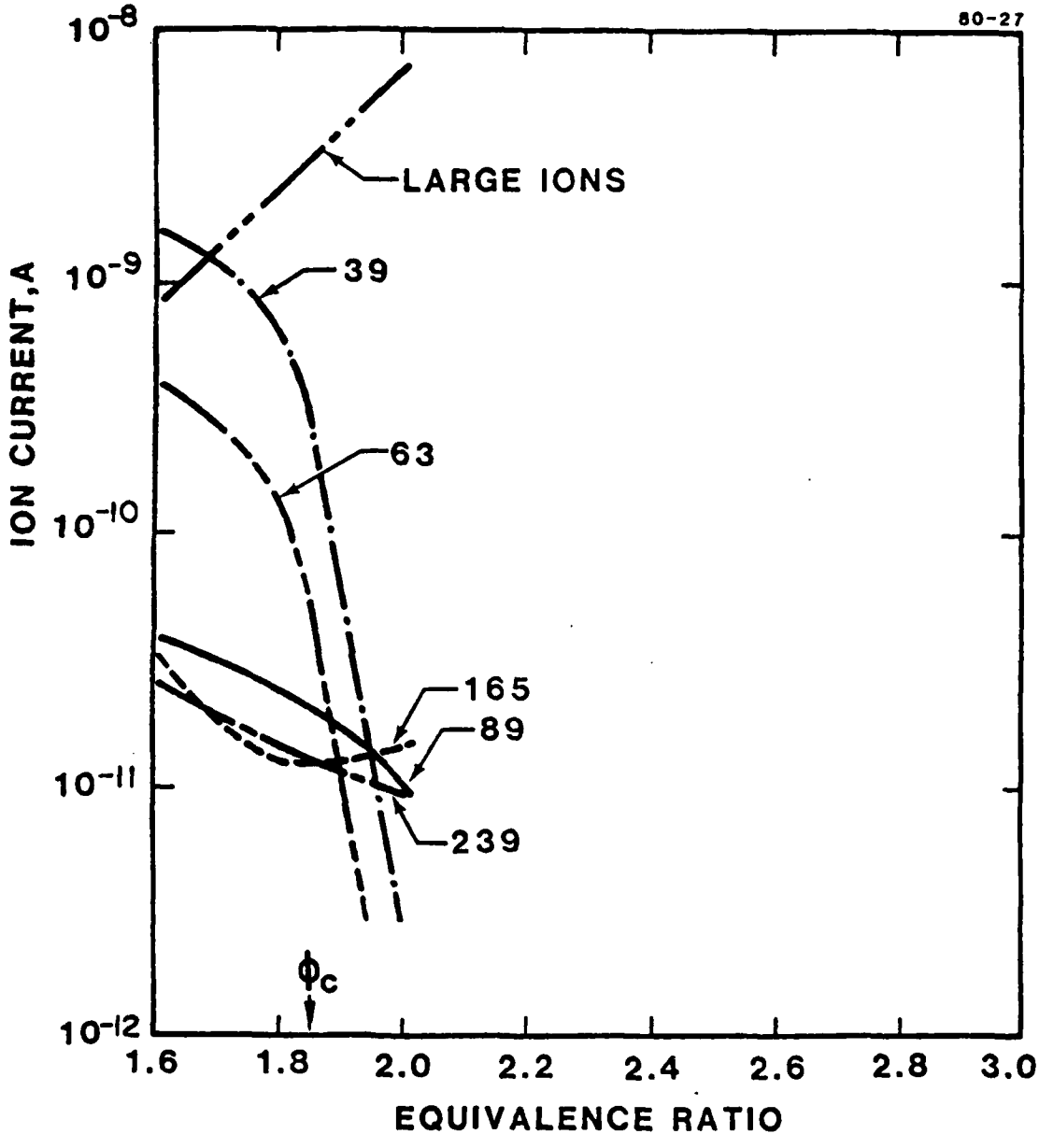

80-27
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
ION CURRENT, A
LARGE IONS
39
63
165
89
239
ϕ_c
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
EQUIVALENCE RATIO

FIG. 7

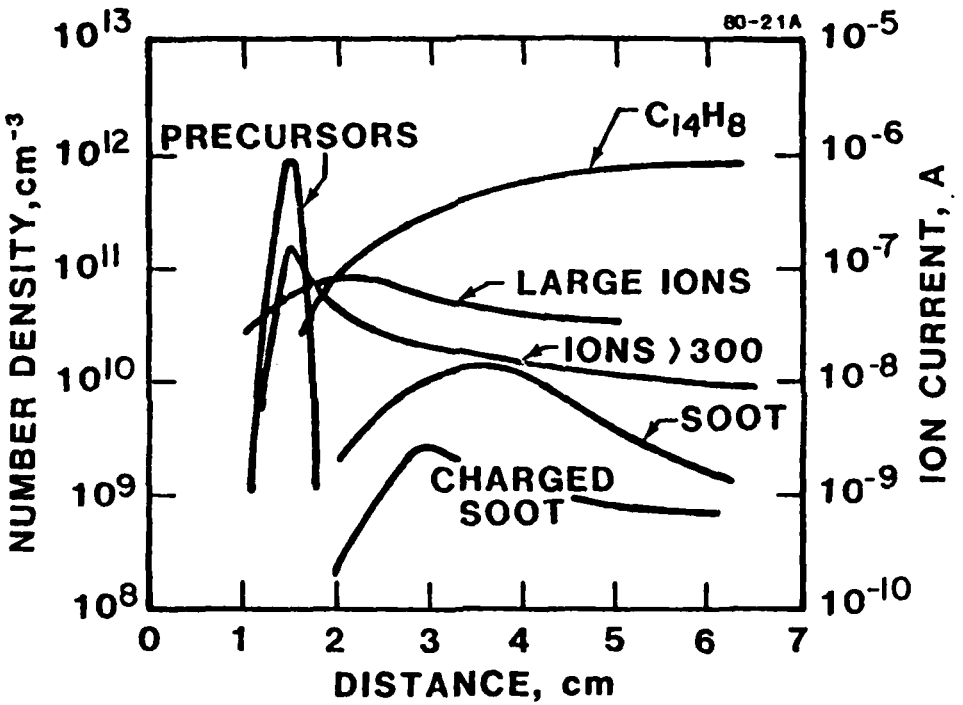

80-21A
NUMBER DENSITY, cm⁻³
ION CURRENT, A
DISTANCE, cm
PRECURSORS
C14H8
LARGE IONS
IONS > 300
SOOT
CHARGED SOOT
10^13
10^12
10^11
10^10
10^9
10^8
10^-5
10^-6
10^-7
10^-8
10^-9
10^-10
0
1
2
3
4
5
6
7

FIG. 8